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1. Untranslatable words are replaced with asterisks (***).
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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1]In one molecule. [two epoxy groups] . [a poly unsaturated polyol compound (c) and a diamine compound (d) which are produced by making an epoxy resin (a) which it has, and a compound (b) which has an unsaturated double bond and one carboxyl group at a time in one molecule react, and a compound (e) which has at least two acid anhydride groups in one molecule] A resin composition containing oligomer (A) produced by making react.

[Claim 2]The resin composition containing a diluent (B), a photopolymerization initiator (C), and a heat curing component (D) according to claim 1.

[Claim 3]A resin composition given in Claims 1-2 a given acid number of oligomer (A) is 10 - 300 mgKOH/g.

[Claim 4]A resin composition given in Claims 1-3 which are the objects for the resists of a printed-circuit board.

[Claim 5]A hardened material of a resin composition given in Claims 1-4.

[Claim 6]An article which has a layer of a hardened material of the resin composition according to claim 5.

[Claim 7]The article according to claim 6 which is a printed wiring board.

[Detailed Description of the Invention]**[0001]**

[Field of the Invention]This invention relates to a resin composition especially the resist ink composition for flexible printed wiring boards, and its hardened material. By the rare alkaline aqueous solution which can be used for a solder resist, plating resist, etc. in the case of flexible printed wiring board manufacture, development is possible in detail and, [the hardened material] It is related with a resin composition suitable for resist ink excellent in flexibility,

folding endurance, adhesion, chemical resistance, a heat-resisting property, etc., a hardened material, and its article.

[0002]

[Description of the Prior Art]In recent years, in various fields, the ultraviolet curing setup-of-tooling product has been used abundantly by the Reasons of saving resources, energy saving, the improvement in workability, a productivity drive, etc. Also in the printed wiring board processing field, various ink, such as solder resist ink and marking ink, shifted to the ultraviolet curing setup-of-tooling product from the conventional heat-curing setup-of-tooling product for the same Reason. For example, to JP,S56-40329,B, the hardenability sensitive material containing the resultant of the epoxy resin-photopolymerization nature alpha, beta-unsaturated-carboxylic-acid addition product, and a dibasicity carboxylic anhydride, a photopolymerization nature monomer, and a photopolymerization initiator is indicated. The type stuck using adhesives after piercing the solder resist used for the polyimide group board called flexible printed wiring board until now by the metal pattern which set the polyimide film called a cover lay film by the pattern, It was a thing of the type which applies the ultraviolet curing type or the heat-curing type solder resist ink which gave flexibility by screen printing. High precision and the demand of high definition increased also to the solder resist for the densification realization accompanying progress in electronics in the common printed wiring board called a rigid (hard) board. In the conventional screen printing, since pattern accuracy is not acquired, the liquefied photoresist method is proposed and it is introduced not less than 50% now.

[0003]

[Problem to be solved by the invention]Although the densification has been required also in the field of a flexible printed wiring board in recent years, Sufficient flexibility or folding endurance are not obtained, and since the paint film of what is obtained is hard and adhesion of pattern accuracy with polyimide is bad, the workability of what is obtained to some extent is bad, and the flexibility of the conventional liquefied photograph solder resist of chemical resistance and a heat-resisting property is insufficient, and a problem in it.

[0004]

[Means for solving problem]In order that this invention persons may solve the aforementioned technical problem, wholeheartedly, [as a result of research] [by using specific oligomer] The development in a rare alkaline aqueous solution is possible, and the resist ink composition for flexible printed wiring boards which excels [heat-resisting property / flexibility, folding endurance, adhesion, chemical resistance,] also in the cured film was found out.

[0005][namely this invention] (1) In one molecule. [two epoxy groups] . [the poly unsaturated polyol compound (c) and diamine compound (d) which are produced by making the epoxy resin (a) which it has, and the compound (b) which has an unsaturated double bond

and one carboxyl group at a time in one molecule react, and the compound (e) which has at least two acid anhydride groups in one molecule] The resin composition, (2) diluents (B) containing the oligomer (A) produced by making react, Containing a photopolymerization initiator (C) and a heat curing component (D) A resin composition the feature and given in ** (1), (3) (1) thru/or the resin composition given in (2) whose acid number of oligomer (A) is 10 - 300 mgKOH/g, (4) It is related with (6) which is the article and (7) printed-wiring board which have a layer of the hardened material of the hardened material of a resin composition a resin composition (1) which is a resist for printed-circuit boards thru/or given in (3), (5) above (1), or given in (4), and a resin composition given in (6) and (5), without the article of a description. [0006][the oligomer (A) used by this invention] In one molecule. [two epoxy groups] It can do, although obtained by making the poly unsaturated polyol compound (c) and diamine compound (d) which are produced by making the epoxy resin (a) which it has, and the compound (b) which has an unsaturated double bond and every one carboxyl group in one molecule react, and the compound (e) which has two acid anhydride groups in one molecule react.

[0007]It is the 1st reaction, and a hydroxyl group is formed of the addition reaction of the epoxy group of an epoxy resin (a), and the carboxyl group of monocarboxylic acid (b), and, specifically, the (c) component is obtained. subsequently, the compound (e) in which the hydroxyl group of (c) and the amino group of (d) have two acid anhydride groups in one molecule and an esterification reaction -- and an amidation reaction is carried out.

[0008]As an epoxy resin (a) which has two epoxy groups, a diglycidyl ether compound, a diglycidyl ester compound, a diglycidyl amine compound, etc. are mentioned into one molecule, for example.

[0009]A diglycidyl ether compound is obtained by the publicly known method to which add 1 Eq or more of latters, and a polyol compound and epichlorohydrin are made to react to 1 Eq of the former hydroxyl groups. As a polyol compound, for example Bisphenol A, the bisphenol F. Bis(4-hydroxyphenyl)ketone, bis(4-hydroxyphenyl)sulfone, Resorcinol, biphenol, tetramethyl biphenol, tetra alkyl biphenol, **** bisphenol A, the **** bisphenol F, tetrabromobisphenol A, Ethylene glycol, diethylene glycol, polyethylene glycol, Propylene glycol, polypropylene glycol, 1,4-butanediol, neopentyl glycol, 1,6-hexandiol, 3-methyl 1,5-pentanediol, 1,9-nonanediol, 1,4-hexanedimethanol, dimer aciddiol, etc. are raised.

[0010]A diglycidyl ester compound is obtained by the publicly known method of making epichlorohydrin 1 Eq or more of latters react to a poly carboxyl compound in addition to 1 Eq of the former carboxyl groups. As a poly carboxyl compound, phthalic acid, a tetrahydrophthalic acid, hexahydrophthalic acid and a methylene tetrahydrophthalic acid, methyl and a methylene tetrahydrophthalic acid, *****, maleic acid, etc. are raised, for example. A diglycidyl amine compound is obtained by making epichlorohydrin 1 Eq or more of latters react to a poly amino

compound in addition to 1 Eq of former amino groups. As a poly amino compound, aniline, o-toluidine, etc. are mentioned, for example.

[0011]Next, as said monocarboxylic acid having unsaturated groups (b), the reactant of acrylic acid, crotonic acid, alpha-cyano cinnamic acid, cinnamic acid, saturation or unsaturated dibasic acid, and an unsaturated group content monoglycidyl compound is mentioned, for example. As acrylic acid, for example The dimer of acrylic acid, methacrylic acid, The half ester which is an equimolar reactant of beta-styryl acrylic acid, beta-furfuryl acrylic acid, saturation, or unsaturated 2 base acid anhydride and the acrylate derivative which has one hydroxyl group in one molecule (meta), The half ester which are the equimolar reactants of saturation or unsaturated dibasic acid, and monoglycidyl (meta) acrylate derivatives is raised.

[0012][as the saturation used for half ester manufacture, or unsaturated 2 base acid anhydride] For example, it is raised in succinic anhydride, maleic anhydride, phthalic anhydride, tetrahydro phthalic anhydride, hexahydro phthalic anhydride, methylhexahydrophthalic anhydride, methyl cyclohexene-dicarboxylic anhydride, itaconic acid anhydride, methyl, and methylene tetrahydro *****. [as acrylate derivatives which have one hydroxyl group in one molecule (meta)] For example, hydroxyethyl (meta) acrylate, hydroxypropyl (meta) acrylate, Hydroxy butyl (meta) acrylate, polyethylene glycol mono-(meta) acrylate, GURISERINJI (meta) acrylate, bird methylol pro pansy (meta) acrylate, pentaerythritol bird (meta) acrylate, dipentaerythritol penta (meta) acrylate, the acrylate (meta) of phenyl glycidyl ether, etc. are raised.

[0013][as the saturation used for another half ester manufacture, or unsaturated dibasic acid] For example, succinic acid, maleic acid, adipic acid, phthalic acid, a tetrahydrophthalic acid, hexahydrophthalic acid, itaconic acid, fumaric acid, etc. are raised, and glycidyl (meta) acrylate etc. are raised as monoglycidyl (meta) acrylate derivatives, for example.

[0014]these monocarboxylic acid having unsaturated groups (b) -- it can be independent, or it can mix and can use. Especially desirable monocarboxylic acid is acrylic acid (meta).

[0015]In order to obtain a poly unsaturated polyol compound (c) used by this invention, Making it react to 1 Eq of an epoxy group of the above-mentioned epoxy resin (a) by above-mentioned monocarboxylic acid having unsaturated groups (b) and a ratio used as about 0.8-1.3 mol makes it react by a ratio which will be about 0.9-1.1 mol preferably desirable especially.

[0016]At the time of a reaction, it is preferred to use a diluent. As a diluent, for example Ketone, such as methyl ethyl ketone and methyl isobutyl ketone, Aromatic hydrocarbon, such as toluene, xylene, and tetramethyl benzene, Glycol ether, such as dipropylene glycol wood ether and dipropylene glycol diethylether, Ester, such as ethyl acetate, butyl acetate, butyl-cellosolve acetate, and carbitol acetate, Lactone, such as gamma-butyrolactone, gamma-valerolactone, and gamma-caprolactone, Alicyclic hydrocarbon, such as aliphatic hydrocarbon, such as octane and Deccan, cyclohexane, and cyclohexanone, Organic solvents, such as

petroleum system solvents, such as light petroleum, petroleum naphtha, **** petroleum naphtha, and solvent naphtha. Or carbitol (meta) acrylate, phenoxyethyl (meta) acrylate, Reactant monomers, such as pentaerythritol tetra (meta) acrylate, trimethylolpropane bird (meta) acrylate, tris (hydroxyethyl) isocyanurate bird (meta) acrylate, and dipentaerythritol hexa (meta) acrylate, are mentioned.

[0017]It is preferred to use a catalyst, in order to promote a reaction. As a catalyst, for example Triethylamine, benzyldimethylamine, Methyl triethyl ammoniumchloride, a benzyl trimethylammonium star's picture, benzyl trimethylammonium iodide, triphenylphosphine, triphenylstibine, chromium octanoate, and zirconium octanoate are raised. The amount of this catalyst used is 0.1 to 10 weight % preferably to a reaction-raw-materials mixture. In order to prevent a polymerization under reaction, it is preferred to use a polymerization inhibitor. As a polymerization inhibitor, hydroquinone, methylhydroquinone, hydroquinone monomethyl ether, catechol, pyrogallol, etc. are raised, for example. The amount used is 0.01 to 1 weight % preferably to a reaction-raw-materials mixture. Reaction temperature is 60-150 ** preferably. Reaction time is 5 to 60 hours preferably.

[0018]Next, although there is no restriction in particular as a diamine compound (d), aromatic diamine, aliphatic diamine, etc. are mentioned, for example.

[0019]As aromatic diamine, it is a 2,2-screw, for example. [4-(4-aminophenoxy) phenyl] Propane, a screw [4-(4-aminophenoxy) phenyl] Sulfone, 2,2-bis- [4-(3-aminophenoxy) phenyl] Hexafluoropropane, a screw [4-(4-aminophenoxy) phenyl] Biphenyl, a screw [4-(4-aminophenoxy) phenyl] Methane, a screw [4-(3-aminophenoxy) phenyl] Methane, a screw [4-(4-aminophenoxy) phenyl] Ether, a screw [4-(3-aminophenoxy) phenyl] Ether, a screw [4-(3-aminophenoxy) phenyl] Benzophenone, a screw [4-(4-aminophenoxy) phenyl] Benzanilide, a screw [4-(3-aminophenoxy) phenyl] Benzanilide, a 9,9-screw [4-(3-aminophenoxy) phenyl] Fluorene, p-phenylenediamine, m-phenylenediamine, p-KISHIRI range amine, m-KISHIRI range amine, 1,5-diaminonaphthalene, 4,4'-benzophenonediamine, etc. are mentioned.

[0020]As aliphatic diamine, for example Ethylenediamine, tetramethylenediamine, Hexamethylenediamine, 1,2-diaminocyclohexane, diaminopolysiloxane, Jeffamine D-230 (made by the following and San Techno Chemical), D-400, D-2000, D-4000, ED-600, ED-900, ED-2001, and EDR-148 grade are mentioned. They can be used for two or more sorts, these being able to be independent or mixing.

[0021][as a polybasic acid anhydride (e) which has at least two acid anhydride groups in a molecule] A carboxylic anhydride's is desirable and For example, pyromellitic dianhydride, benzophenone tetracarboxylic dianhydride, Biphenyl tetracarboxylic dianhydride, biphenyl ether tetracarboxylic dianhydride, Diphenylsulfone tetracarboxylic dianhydride, butane tetracarboxylic dianhydride, ethyleneglycol bis(anhydrotrimellitate), etc. are mentioned, and two or more sorts can be used, being able to be independent or mixing.

[0022]Next, in order to make the poly unsaturated polyol compound (c) and diamine compound (d) which were obtained above, and the compound (e) which has at least two acid anhydride groups in one molecule react and to manufacture oligomer (A), There are a method to which these are made to react simultaneously, and a method to which (c) is made to react after making (e) react to (d) and compounding a polyamide prepolymer. As a method of making it react simultaneously, when the sum total equivalent of the hydroxyl group of said poly unsaturated polyol compound (c) and the amino group of a diamine compound (d) is 1 Eq, it is preferred to make 0.1-0.9 Eq (considering it as an acid anhydride equivalent) of compounds (e) which have two acid anhydride groups in one molecule react. As for 0-150 °C and reaction time, 1 to 10 hours is preferred, and reaction temperature may add catalysts, such as triethylamine, 0.1 to 10%.

[0023][a polyamide prepolymer] [as a method to which an after-synthesis poly unsaturated polyol compound (c) is made to react] First, a diamine compound (d) and the polybasic acid anhydride (e) which has at least two acid anhydride groups in a molecule are made to react, an end acid anhydride polyamide prepolymer (f) is prepared, and, subsequently a poly unsaturated polyol compound (c) is made to react.

[0024]As for an end acid anhydride polyamide prepolymer (f), it is preferred to make 1.05-2.05 Eq react (as an acid anhydride equivalent) of the polybasic acid anhydride (e) which has at least two acid anhydride groups in a molecule to 1 Eq of amino groups of a diamine compound (d). As for 0-80 °C and reaction time, 1 to 10 hours is [the reaction temperature of this amidation reaction] usually preferred.

[0025]Subsequently, a poly unsaturated polyol compound (c) is made to react to an end acid anhydride polyamide prepolymer (f), and oligomer (A) is obtained. It is 0.1-0.8 Eq to make 0.05-0.95 Eq of acid anhydride groups of an end acid anhydride polyamide prepolymer react to 1 Eq of hydroxyl groups of a poly unsaturated polyol compound (c) desirable especially preferably. Reaction temperature is ordinary temperature -100 °C, and is usually 50-90 °C preferably. In order to prevent the gelling by a radical polymerization during this reaction, it is usually preferred to add polymerization inhibitor, such as 50-2000 ppm hydroquinone, hydroquinone monomethyl ether, p-methoxy phenol, and p-benzoquinone. Although the reaction of these hydroxyl groups and an acid anhydride group advances with a non-catalyst, basic compounds, such as triethylamine and triphenylphosphine, may be added as a catalyst.

[0026]A diluent may be added at the time of this reaction. As a diluent, for example Ketone, such as methyl ethyl ketone and methyl isobutyl ketone, Aromatic hydrocarbon, such as toluene, xylene, and tetramethyl benzene, Glycol ether, such as dipropylene glycol wood ether and dipropylene glycol diethylether, Ester, such as ethyl acetate, butyl acetate, butyl-cellosolve acetate, and carbitol acetate, Lactone, such as gamma-butyrolactone, gamma-valerolactone, and gamma-caprolactone, Alicyclic hydrocarbon, such as aliphatic hydrocarbon, such as

octane and Deccan, cyclohexane, and cyclohexanone, Organic solvents, such as petroleum system solvents, such as light petroleum, petroleum naphtha, **** petroleum naphtha, and solvent naphtha. Or carbitol (meta) acrylate, phenoxyethyl (meta) acrylate, Reactant monomers, such as pentaerythritol tetra (meta) acrylate, trimethylolpropane bird (meta) acrylate, tris (hydroxyethyl) isocyanurate bird (meta) acrylate, and dipentaerythritol hexa (meta) acrylate, are mentioned.

[0027]As for the quantity of the oligomer (A) contained in the resin composition of this invention, 10 to 100 weight % is preferred among a constituent, and its 15 to 100 weight % is especially preferred.

[0028]In this invention, a diluent (B), a photopolymerization initiator (C), and a heat curing component (D) may be contained. As a diluent (B), an organic solvent and/or a photopolymerization nature monomer can be used, for example. As a typical thing of an organic solvent, for example Ketone, such as methyl ethyl ketone and methyl isobutyl ketone, Aromatic hydrocarbon, such as toluene, xylene, and tetramethyl benzene, Glycol ether, such as dipropylene glycol wood ether and dipropylene glycol diethylether, Ester, such as ethyl acetate, butyl acetate, butyl-cellosolve acetate, and carbitol acetate, Lactone, such as gamma-butyrolactone, gamma-valerolactone, and gamma-caprolactone, Petroleum system solvents, such as alicyclic hydrocarbon, such as aliphatic hydrocarbon, such as octane and Deccan, cyclohexane, and cyclohexanone, light petroleum, petroleum naphtha, **** petroleum naphtha, and solvent naphtha, etc. can be mentioned.

[0029]On the other hand, [as a typical thing of a photopolymerization nature monomer] Hydroxyalkyl (meta) acrylate, such as 2-hydroxyethyl (meta) acrylate and 2-hydroxypropyl (meta) acrylate, Mono- ** of glycols, such as ethylene glycol, methoxy tetraethylene glycol, and polyethylene glycol, di(meth)acrylate, Acrylamide, such as N,N-dimethyl(meta) acrylamide and N-methylol(metha)acrylamide (meta), Amino alkyl (meta) acrylate, such as N,N-dimethylaminoethyl (meta) acrylate, Hexandiol, trimethylolpropane, pentaerythritol, Polyhydric alcohols, such as ditrimethylol propane, dipentaerythritol, and tris-hydroxyethyl isocyanurate. Or such ethyleneoxides or multivalent (meta) acrylate of a propylene oxide addition product, The ethyleneoxide of phenols, such as phenoxyethyl (meta) acrylate and poly ETOKISHIJI (meta) acrylate of bisphenol A, or the acrylate (meta) of a propylene oxide addition product, glycerol diglycidyl ether, The acrylate of glycidyl ether, such as trimethylolpropane triglycidyl ether and triglycidyl isocyanurate (meta), epsilon-caprolactone denaturation (meta) acrylate, melamine (meta) acrylate, etc., such as caprolactone denaturation tris (acryloxyethyl) isocyanurate, can be mentioned.

[0030]The aforementioned diluent (B) can be used as independent or two or more sorts of mixtures. 5 - 400 weight section is desirable especially preferred to (A) component 100 weight section, and the quantity of a diluent (B) is 10 - 250 weight section.

[0031]The purpose of using said diluent (B) in the case of a photopolymerization nature monomer, (A) It is for carrying out film formation more to dilute a component, to change into the state of being easy to apply, and to enhance photopolymerization nature, for the case of an organic solvent to make the (A) component dissolve and dilute, to apply it as liquefied by it, and to make it dry subsequently. Therefore, according to the diluent to be used, the exposure method of either [which contacts a photomask to a paint film] a contact method or a non-contact method is used.

[0032]As a photopolymerization initiator (C), for example Benzoin, benzoin methyl ether, Benzoin, such as benzoin iso-propyl ether, acetophenone, 2,2-dimethoxy- 2-phenylacetophenone, 2,2-diethoxy- 2-phenylacetophenone, 1,1-dichloro acetophenone, 1-hydroxy cyclohexyl phenyl ketone, 2-methyl- 1 - [4-(methylthio) phenyl] Acetophenone, such as 2-morpholino propane-1-ON and N,N-dimethylamino acetophenone, 2-methylanthraquinone, 2-ethylanthraquinone, 2-tert-butyl anthraquinone, Anthraquinone, such as 1-chloro anthraquinone, 2-amyl anthraquinone, and 2-aminoanthraquinone, A 2,4-dimethyl thioxan ton, 2, 4-diethylthio xanthone, Thioxan tons, such as 2-chloro thioxan ton and a 2,4-diisopropyl thioxan ton, Ketals, such as acetophenone dimethyl ketal and benzyl dimethyl ketal, Benzophenone, methylbenzophenone, 4,4'-dichloro benzophenone, 4,4'-screw diethylamino benzophenone, MIHIRAZU ketone, There are benzophenone [, such as 4-benzoyl-4'-methyldi phenyl sulfide,], 2 and 4, and 6-bird methylbenzoyl diphenylphosphine oxide etc., and it can be independent or can use combining two or more sorts.

[0033]Desirable combination is the 2-methyl- 1. - [4-(methylthio) phenyl] -2-morpholino propane-1-ON (the Ciba-Geigy make, IRGACURE 907) and 2 and 4-diethylthio xanthone (the Nippon Kayaku Co., Ltd. make.) It is combination with the kaya cure DETX, 2-isopropyl thioxan ton, or 4-benzoyl-4'-methyldi phenyl sulfide, etc.

[0034]0.5 - 20 weight section is desirable especially preferred to component 100 nonvolatile weight section of the resin composition of this invention, and the use rate of a photopolymerization initiator (C) is 1 - 10 weight section.

[0035]To a photopolymerization initiator (C), N and N-dimethylaminobenzoic acid ethyl ester, A photosensitizer like the third class amine, such as N,N-dimethylamino isoamyl benzoate ester, pentyl 4-dimethylamino benzoate, triethylamine, and triethanolamine, can be used in combination with independent or two sorts or more. The amount used is usually about 0.1-20 weight sections to component 100 nonvolatile weight section of a resin composition.

[0036]A heat curing component (D) can be used in this invention. By using this, solder heat resistance and an electrical property can be raised further. As a heat curing component (D) which can be used, an epoxy resin, a melamine compound, an oxazoline compound, phenol system resin, etc. can be mentioned. As an epoxy resin, for example A bisphenol A type epoxy resin, bisphenol F type epoxy resin, Phenol novolak type epoxy resin, cresol novolak type

epoxy resin, Glycidylethers; 3,4-epoxy-6-methylcyclohexyl methyl-3,4-epoxy-6-methylcyclohexane carboxylate, such as a trisphenol methane type epoxy resin, brominated epoxy resin, and a biphenol type epoxy resin, 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexane carboxylate, Cycloaliphatic epoxy resin, such as 1-epoxy ethyl-3,4-epoxy cyclohexane; Phthalic acid diglycidyl ester, Glycidyl amine, such as glycidyl ester; tetraglycidyl ether diaminodiphenylmethanes, such as tetrahydrophthal acid diglycidyl ester and dimer acid glycidyl ester; heterocyclic epoxy resins, such as triglycidyl isocyanurate, etc. are mentioned. Especially, a not less than 50 ** epoxy resin can form a photopolymerization sexual skin film without after-desiccation tackiness, and its melting point is preferred.

[0037]As a melamine compound, the melamine resin which is a polycondensation thing of melamine, melamine, and formalin is mentioned. As a urea compound, the urea resin etc. which are the polycondensation things of urea, urea, and formalin are mentioned.

[0038]As an oxazoline compound, 2-oxazoline, 2-methyl-2-oxazoline, 2-phenyl-2-oxazoline, 2,5-dimethyl- 2-oxazoline, 5-methyl-2-phenyl-2-oxazoline, 2,4-diphenyl oxazoline, etc. are mentioned.

[0039]as phenol system resin -- phenol and cresol -- it goes berserk and NORU, catechol, resorcinol, hydroquinone, pyrogallol, resol, etc. are mentioned. Since it says that it excels in reactivity with the carboxyl group in the (A) component also in these heat curing components (D), and excels also in adhesion with copper, an epoxy resin is preferred. As for a heat curing component (D), it is preferred to carry out [from which the functional group per carboxyl group in the (A) component and in a heat curing component (D) will be 0.2-3 Eq] quantity use. Since it says that hardening good for the solder heat resistance at the time of especially using a printed wiring board or an electrical property is given, 1.0-1.5 Eq is preferred.

[0040]When using an epoxy resin as the above-mentioned heat curing component (D), it is preferred to use a hardening accelerator. As a hardening accelerator of an epoxy resin, for example 2-methylimidazole, 2-ethyl-3-methylimidazole, 2-undecylimidazole, 2-phenylimidazole, 1-cyano ethyl-2-ethylimidazole, Imidazole compounds, such as 1-cyano ethyl-2-undecylimidazole, Melamine, guanamine, acetoguanamine, benzoguanamine, ethyldiaminotriazine, 2,4-diaminotriazine, 2,4-diamino-6-tolyl triazine, The third class amine, such as triazine derivatives, such as 2,4-diamino-6-xylyl triazine, trimethylamine, triethanolamine, N,N-dimethyl octylamine, pyridine, and m-aminophenol, and polyphenol are mentioned. They can be used, these hardening accelerators being able to be independent or using them together.

[0041]10-300 are desirable especially preferred, and the acid numbers (mgKOH/g) of the oligomer (A) used by this invention are 50-200.

[0042]Further, the resin composition of this invention characteristics, such as adhesion and hardness, if needed in order to improve Barium sulfate, Inorganic bulking agents, such as

barium titanate, silicon-oxide powder, a fine-powder-form silicon oxide, amorphous silica, a talc, clay, magnesium carbonate, calcium carbonate, aluminium oxide, aluminium hydroxide, and mica powder, can be used. 0 to 60 weight % in the constituent of this invention is desirable especially preferred, and the amount used is 5 to 40 weight %.

[0043]If needed Copper phthalocyanine blue, Phthalocyanine Green, AIOJIN green, Diarylide Yellow, Crystal Violet, Colorants, such as titanium oxide, carbon black, and naphthalene black, Hydroquinone, hydroquinone monomethyl ether, tert-butyl catechol, A defoaming agent and/, such as thickeners, such as polymerization inhibitor, such as pyrogallol and phenothiazin, asbestos, Orr Ben, Benton, and montmorillonite, a silicone series, a fluorine system, and a polymer system. Or the additives like adhesion grant agents, such as a leveling agent, an imidazole series, a thiazole system, a triazole series, and a silane coupling agent, can be used.

[0044]The copolymers of ethylenic unsaturated compounds, such as acrylic ester, Binder resin and polyester (meta) acrylate, such as polyhydric alcohols and polyester resin which are compounded from a polybasic acid compound, Photopolymerization nature oligomer, such as polyurethane (meta) acrylate and epoxy (meta) acrylate, can be used in the range which does not have on the various characteristics as a solder resist.

[0045]Water can also be added for the fall of the inflammability of the resin composition of this invention. In adding water, the carboxyl group of the (A) component Trimethylamine, Amine [, such as triethylamine,], N, and N-dimethylaminoethyl (meta) acrylate, N,N-dimethylaminopropyl (meta) acrylamide, N,N-dimethyl(meta) acrylamide, It is preferred to make it dissolve the (A) component in water by carrying out salt formation with the acrylate compound which has the 3rd class amino groups, such as acryloyl morpholine, N-isopropyl (meta) acrylamide, and N-methylolacrylamide (meta).

[0046]The resin composition of this invention blends the above-mentioned combination component at a desirable aforementioned rate, and is obtained by mixing uniformly by a roll mill etc.

[0047]The resin composition of this invention is liquefied, and is useful as resist ink, and can be used also as a coating material, a coating agent, adhesives, etc.

[0048]The hardened material of this invention stiffens the resin composition of above-mentioned this invention by the active-light exposure of ultraviolet radiation etc. Hardening by the active-light exposure of ultraviolet radiation etc. can be performed with a conventional method. For example, what is necessary is just to use ultraviolet ray generators, such as a low pressure mercury lamp, a high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, xenon light, and ultraviolet radiation luminescence lasers (excimer laser etc.), when irradiating with ultraviolet radiation. The hardened material of the resin composition of this invention is used for the electricity and electronic parts like a printed circuit board as an

insulating material between layers for a permanent resist or build-up construction methods, for example. As for the thickness of this hardened material layer, about 1-60 micrometers is usually preferred at about 0.5-160 micrometers.

[0049]The printed wiring board of this invention can be obtained as follows, for example. Namely, the resin composition of this invention is adjusted to the viscosity which was suitable for the coating method if needed, To the flexible printed wiring board by which circuit formation was carried out, for example, screen printing, By methods, such as a spray method, the roll coat method, electrostatic spray painting, and the curtain coat method, usually 0.5-160 micrometers, After applying the resin composition of this invention by 1-60-micrometer thickness preferably and drying a paint film at 60-110 **, a negative film is directly contacted to a paint film (.). [or for improvement in various physical properties after / which is kept on a paint film in the state where it does not contact / irradiating with an active light subsequently and carrying out dissolution removal (development) of the unexposed portion by rare alkaline aqueous solutions (for example, 0.5 to 2% sodium carbonate aqueous solution etc.)] With an exposure and/or heating (it is 0.5 to 1.0 hour at 100-200 **) of an active light, sufficient hardening is performed and a cured film is obtained. Thereby, various characteristics, such as the heat-resisting property of the resist layer excellent in flexibility, solvent resistance, acid resistance, adhesion, and an electrical property, can be made to improve. As an active light, ultraviolet radiation, a visible radiation, etc. are raised, for example. As a source of an active light, low pressure or a high-pressure mercury-vapor lamp, xenon light, etc. are raised, for example.

[0050]As an alkaline aqueous solution used for the above and development, rare alkaline aqueous solutions, such as potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate, sodium phosphate, sodium silicate, ammonia, and amine, are raised, for example. As a source of irradiation light for carrying out optical hardening, a low pressure mercury lamp, an inside pressure mercury-vapor lamp, a high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, a xenon lamp, or a metal halide lamp is suitable. In addition, a laser beam etc. can be used as active light for exposure.

[0051]

[Working example]Hereafter, the work example of this invention explains still more concretely. it comes out that this invention is not what is limited to the following work example from the first. The part in a work example is a weight section.

[0052]The synthetic example 1 (synthesis 1 of a poly unsaturated group polyol compound (c)) a round bottom flask with a stirring device and a condenser tube -- bisphenol F type epoxy resin (name-of-article: -- YDF-8170C.) The Tohto Kasei Co., Ltd. make 500g, the acrylic acid 224.2g, 3.62 g of triphenylphosphine, and 0.72 g of methoxy phenol were taught, **** and after dissolving, it reacted to 60 ** at 98 ** for 24 hours, and the poly unsaturated polyol (c-1) of acid

number 0.3 mgKOH/g was obtained.

[0053]The synthetic example 2 (synthesis 2 of a poly unsaturated group polyol compound (c)) To a round bottom flask with a stirring device and a condenser tube, 168.2 g of mixtures (a name of article: ZX-1059, Tohto Kasei Co., Ltd. make) of a bisphenol A type epoxy resin and bisphenol F type epoxy resin, The acrylic acid 72.06g, 1.2 g of triphenylphosphine, and 0.24 g of methoxy phenol were taught, **** and after dissolving, it reacted to 60 ** at 98 ** for 24 hours, and a poly unsaturated polyol (c-2) of acid number 0.3 mgKOH/g was obtained.

[0054]The synthetic example 3 (synthesis of an end acid anhydride polyamide prepolymer (f)) To a round bottom flask with a stirring device and a condenser tube, the 3,4'-diaminophenyl ether 200.2g, 436 g of pyromellitic dianhydride (a name of article: PMDA, Mitsubishi Gas Chemical Co., Inc. make) and the gamma-butyrolactone 636.2g were prepared, it reacted at 40 ** for about 5 hours, and solid content acid number 519.6 mgKOH/g and an end acid anhydride polyamide prepolymer (f-1) of 50% of solid content were obtained.

[0055]The synthetic example 4 (synthesis 1 of oligomer (A)) 456.5 (c-1) g obtained in the synthetic example 1 by round bottom flask with a stirring device and a condenser tube, The 3,4'-diaminophenyl ether 50g, pyromellitic dianhydride (a name of article:) [PMDA and] The Mitsubishi Gas Chemical Co., Inc. make 109g and the gamma-butyrolactone 410g were prepared, and it ****(ed) at 5 hours and also 98 ** at 40 **, and reacted for 24 hours, and solid content acid number 89.5 mgKOH/g and oligomer (A-1) of 60% of solid content were obtained.

[0056]The synthetic example 5 (synthesis 2 of oligomer (A)) 470.6 (c-2) g obtained in the synthetic example 2 by the round bottom flask with a stirring device and a condenser tube, The 3,4'-diaminophenyl ether 50g, pyromellitic dianhydride (name of article:) [PMDA and] The Mitsubishi Gas Chemical Co., Inc. make 109g and the gamma-butyrolactone 420.3g were prepared, and it ****(ed) at 5 hours and also 98 ** at 40 **, and reacted for 24 hours, and solid content acid number 87.5 mgKOH/g and oligomer (A-2) of 60% of solid content were obtained.

[0057]The synthetic example 5 (synthesis 3 of oligomer (A)) The 763.4 (f-1)g gamma-butyrolactone 186.5 obtained in 470.6 (c-2) g obtained in the synthetic example 2 and the synthetic example 3 is taught to a round bottom flask with a stirring device and a condenser tube, **** and after dissolving, it reacted to 60 ** at 98 ** for 24 hours, and solid content acid number 116.4 mgKOH/g and oligomer (A-3) of 60% of solid content were obtained.

[0058]The constituent was blended according to the combination presentation (a numerical value is a weight section) shown in the one to work-examples 1-3 and comparative example 2 table 1, and it kneaded and prepared by 3 roll mills. This with screen printing, It applied to the copper-clad polyimide film board (copper thickness / 12micrometer and polyimide film

thickness / 25micrometer) by which pattern formation is carried out so that it may become a thickness of 20-30 micrometers using the polyester screen of 100 meshes completely, and the paint film was dried with an 80 ** air forced oven for 30 minutes. Subsequently, the negative film which has a resist pattern was stuck to the paint film, and it irradiated with ultraviolet radiation using ultraviolet radiation exposure device ORC Manufacturing Co., Ltd., and form HMW-680GW (light exposure $500\text{mJ}/\text{cm}^2$). Next, negatives were developed with the spray pressure of $2.0\text{ kg}/\text{cm}^2$ for 60 seconds in 1% of sodium carbonate aqueous solution, and dissolution removal of the unexposed portion was carried out. About what was obtained, evaluation of development nature and optical sensitivity was performed as below-mentioned. Then, the examination of adhesion, pencil hardness, solvent resistance, acid resistance, a heat-resisting property, tropism-proof, and folding endurance was done as below-mentioned about the specimen which has the hardening layer obtained by performing heating hardening for 40 minutes with a 150 ** air forced oven. Those results are shown in Table 1. A test method and the valuation method are as follows.

[0059](Development nature) The following valuation basis was used.

O ** which ink was completely removed and has been developed at the time of development What [has residue slightly at the time of development] x There is a portion which is not developed at the time of development. [0060](Optical sensitivity) 21 steps (made by SUTOFA) of step tablets were stuck to the paint film after desiccation, and exposure exposure of the ultraviolet radiation of addition quantity-of-light $500\text{ mJ}/\text{cm}^2$ was carried out. Next, the number of stages of the paint film which developed negatives with the spray pressure of $2.0\text{ kg}/\text{cm}^2$ for 60 seconds in 1% of sodium carbonate aqueous solution, and remained without developing negatives was checked.

O More than nine step ** 6 - 8 step x Five or less steps [0061](Adhesion) According to JIS K5400, the peeling examination was done for eye 1-mm **** on the specimen with the 100 piece making-Scotch tape, the desquamative state of eye **** was observed, and the following basis estimated.

O What [does not have peeling at 100/100] ** 50/100-99/100x 0 / 100 - 49/100

[0062](Pencil hardness) It evaluated according to JIS K5400.

[0063](Solvent resistance) The specimen was immersed in isopropyl alcohol for 30 minutes at the room temperature. After checking whether there are any abnormalities in appearance, the peeling examination by a Scotch tape was done and the following basis estimated.

O What [does not have abnormalities in paint film appearance and has neither blistering nor exfoliation] x What has blistering and exfoliation in a paint film [0064](Acid resistance)

The specimen was immersed in the hydrochloric acid aqueous solution at the room temperature 10% for 30 minutes. After checking whether there are any abnormalities in

appearance, the peeling examination by a Scotch tape was done and the following basis estimated.

O What [does not have abnormalities in paint film appearance and has neither blistering nor exfoliation] x What has blistering and exfoliation in a paint film [0065](Heat-resisting property) Rosin system flux was applied to the specimen and it was immersed in a 260 ** solder tub for 5 seconds. This is made into one cycle and it is 3 cycle *****. After cooling radiationally to a room temperature, the peeling examination by a Scotch tape was done and the following basis estimated.

O What [does not have abnormalities in paint film appearance and has neither blistering nor exfoliation] x What has blistering and exfoliation in a paint film [0066](Flexibility) It carried out according to JIS K5400. Using the specimen, the diameter of the axis was 2 mm and observed the existence of the crack generation.

O With no crack.

x The crack went into the bent part and the hardening layer exfoliated.

[0067](Folding endurance) It carried out according to JIS K5016. The curvature radius of the bending side was 0.38 mm, and measured the number of times of bending until a crack enters.

O More than 1000 times x 1 time [0068]

Table 1 Fruit ** An example A ratio ** Example 1 2 3. 1 Oligomer (A-1) obtained in example 4 of 2 synthesis. Oligomer (A-2) obtained in the example 5 of 69 synthesis. Oligomer (A-3) obtained in the example 3 of 69 synthesis. 69KAYARAD ZBR *1 69KAYARAD. PCR *2 69KAYARAD DPHA*3. 3.5 3.5 3.5 3.5 3.5 IRGACURE 907*4 3.0 3.0 3.0 3.0 3.0 KAYACURE DETX-S*5 0.5 0.5 0.5 0.5 0.5 KAYACURE BMS*6 1.0. 1.0 1.0 1.0 1.0 EXA-4800. *7 10.0 10.0 10.0 10.0. 10.0 dicyandiamide (epoxy curing agent). 0.5 0.5 0.5 0.5 0.5 silica (inorganic bulking agent) -- 10.0 10.0 10.0 10.0 10.0 Phthalocyanine Green (pigment) -- 0.5 0.5 0.5 0.5 0.5 Aerosil #200 *8. 1.0 1.0 1.0 1.0 1.0 MODAFURO *9 1.0 1.0 1.0 1.0 1.0 -----

Development nature O O O ** O optical sensitivity O O O x O adhesion O O O O O pencil

hardness 5H 5H 5H 4H 7H flexibility O O O O x folding endurance O O O O x solvent

resistance O O O x O acid resistance An O O O x O heat-resisting property O O O x O [0069]

Notes

KAYARAD ZBR- : *1) It is the thing which made succinic anhydride react to the Nippon Kayaku Co., Ltd. make and bisphenol A type epoxy acrylate (thing which made acrylic acid react to the product made from Oil recovery Shell Epoxy, and Epicoat 1004), 24.5 weight % of carbitol acetate and 10.5 weight % of solvent naphtha contain, and, [the acid number of solid content] *2 KAYARAD PCR- which is 100 mgKOH/g; The Nippon Kayaku Co., Ltd. make, It is the thing which made succinic anhydride react to phenol novolak type epoxy acrylate (the Nippon Kayaku Co., Ltd. make, thing which made acrylic acid react to EPPN-201), 24.5 weight % of

carbitol acetate and 10.5 weight % of solvent naphtha contain, and, [the acid number of solid content] Mixture *4 IRGACURE 907 of *3KAYARAD DPHA:Nippon Kayaku [Co., Ltd.] make, dipentaerythritol penta, and hexa acrylate which is 100 mgKOH/g: The Ciba-Geigy make, photopolymerization initiators, 2-methyl- [4-(methylthio) phenyl] -2-morpholino 1-propanone *5 KAYACURE DETX-S : The Nippon Kayaku Co., Ltd. make, A photopolymerization initiator, 2, 4-diethylthio xanthone *6KAYACURE BMS : The Nippon Kayaku Co., Ltd. make, Photopolymerization initiator and 4-benzoyl-4'-methylphenyl sulfide *7EXA-4800 : The product made from Dainippon Ink Industry, The product made from bisphenol S type epoxy-resin *8 Aerosil #200:Japan Aerosil, silica [anhydrous] *9 MODAFURO: The Monsanto Co. make, a leveling agent [0070]The resist ink composition of this invention and its hardened material are excellent in development nature and photosensitivity, and it is clear the hardened material's to excel in flexibility, folding endurance, solvent resistance, acid resistance, a heat-resisting property, etc. so that clearly from the evaluation result of Table 1.

[0071]

[Effect of the Invention]In formation of the solder resist pattern by the thing in which the resist ink composition of this invention let the film in which the pattern was formed pass and for which it exposes by ultraviolet radiation alternatively and an unexposed portion is developed, The hardened material obtained by excelling in development nature and optical sensitivity is excellent in flexibility and folding endurance, and fully satisfies adhesion, pencil hardness, solvent resistance, acid resistance, a heat-resisting property, etc. In particular, it is suitable for the liquefied solder resist ink composition for flexible printed wiring boards.

[Translation done.]